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Organic Emissions from Consumer Products to the Indoor Environment

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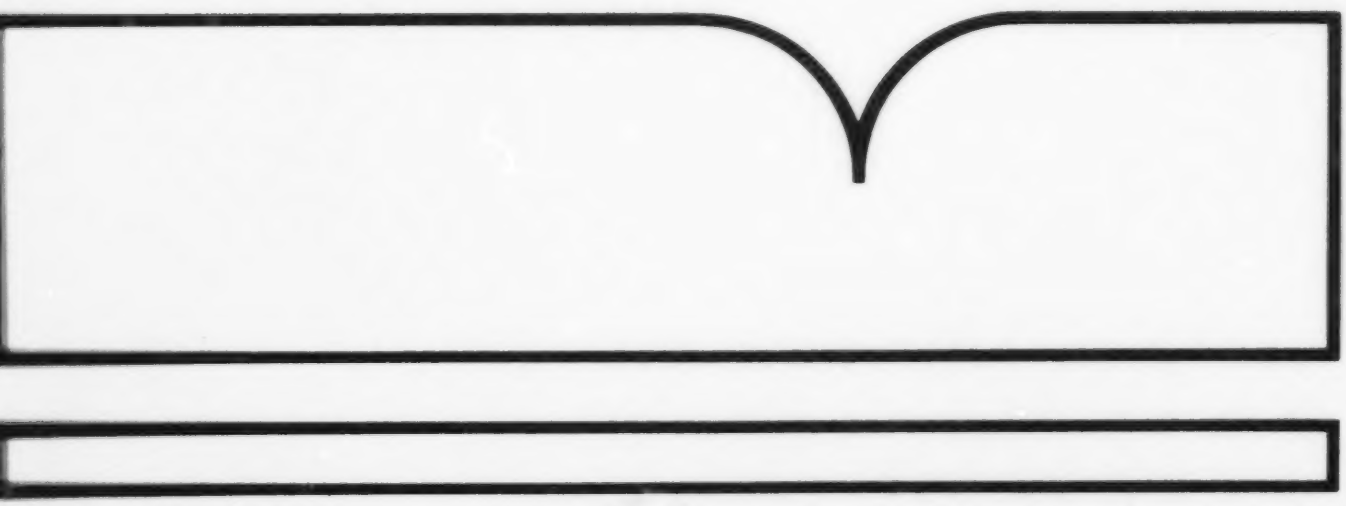

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ORGANIC EMISSIONS FROM CONSUMER PRODUCTS TO THE INDOOR ENVIRONMENT

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16. ABSTRACT The paper discusses EPA studies in small environmental test chambers on a variety of building materials and consumer products. A number of test conditions are critical in effectively determining emission rates (e.g., temperature, humidity, air exchange rate, and product loading--area of sample/volume of test chamber). In addition, the effects of chamber concentration and chamber wall effects (i.e., adsorption to and desorption from surfaces) need to be determined. Finally, the age and condition of the sample affect its emission rate. All of these variables and phenomena are considered in the EPA research program.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Emission	Stationary Sources	14G
Organic Compounds	Indoor Air	07C
Construction Materials	Consumer Products	13C
Atmosphere Contamination Control		06K
Residential Buildings		13M

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INTRODUCTION

Various studies of indoor air quality (IAQ) have identified more than 250 different organics at levels greater than 1 ppb.[1] Many hundreds of additional compounds undoubtedly exist at lower levels. Individual researchers commonly measure 30 - 50 separate compounds.[2,3,4,5] An evaluation of the data reported in such studies indicates:

a. An extremely wide variety of organic compounds are found in indoor air.

b. The range of measured concentrations between different organic compounds is extremely wide, often two or more orders of magnitude; also, the range of concentrations for a specific compound can vary widely between measurements.

c. In most cases, the concentrations of specific organic compounds exceed the outdoor concentration, thus indicating that the source of the compounds is indoors.

d. The sources of the organic compounds are quite numerous within any indoor environment; the sources vary depending on the type of building studied.

To develop source specific emissions data, EPA's Air and Energy Engineering Research Laboratory in Research Triangle Park, North Carolina, is conducting studies in small environmental test chambers on a variety of building materials and consumer products. A number of test conditions are critical to an effective determination of emission rates, including: temperature, humidity, air exchange rate, and product loading (area of sample/volume of test chamber). In addition, the effects of chamber concentration and chamber "wall effects" (i.e., adsorption to and desorption from surfaces) need to be determined. Finally, the age and condition of the sample affect its emission rate. All of these variables and phenomena are considered in the EPA research program.

SOURCES OF INDOOR ORGANIC VAPORS

Many indoor materials, including paints, stains, adhesives, and caulks, contain petroleum-based solvents. Such solvents consist of a variety of organic compounds which are often found in indoor environments. All general surveys of indoor air quality have detected solvent-based compounds, and there is consistency between the surveys in the detection of specific organics. For example, 22 of the same organic species were identified by Molhave[4] among 52 compounds emitted from common building materials and by Seifert et al.[5] among 43 compounds detected in public buildings in West Germany. Chlorinated solvents are also used in a wide variety of consumer products and are commonly

found in indoor air. For example, an EPA study by Midwest Research Institute[6] determined the chlorocarbon content of more than 1100 household products, including shoe polishes, water repellents, cleaning fluids, epoxy paint sprays, brush cleaners, primers, stains, and varnishes. Table I indicates the variety of compounds that are emitted from widely used solvents. This table illustrates the complexity of the organic emissions from solvents in indoor materials; it is not an exhaustive list of all solvent-based organics.

Note that many of the compounds in Table I are not exclusively emitted from solvents. For example, gasoline vapors from attached garages and stored fuel may contribute significant quantities of benzene, xylene, and other hydrocarbons; outgassing from chlorinated water is a source of trichloroethylene and other halogenated organics; and perchloroethylene is emitted from dry cleaned clothes.[7]

While solvent-based indoor emissions come from an extremely wide variety of materials and products, other organic vapors can be associated more closely with specific sources. Table II lists specific compounds and their associated sources. As above this table is not all inclusive, but does illustrate a variety of organic vapor sources.

EXPERIMENTAL METHODS

Laboratory Facility

EPA's Indoor Air Source Characterization Laboratory has been described in detail in previous papers.[8,9,10] The facility consists of the following components: a clean air conditioning and delivery system, an incubator containing two 166 liter environmental test chambers, sampling manifolds, and sample collection adsorbers using Tenax and charcoal. A permeation system for quality control is included. The environmental variables are monitored and controlled via microcomputer. Organic analyses are conducted by thermal desorption, concentration via purge and trap, and gas chromatography (GC) using flame ionization detectors (FID). A separate microcomputer provides GC data analysis. All data are input to spreadsheets for further analysis.

Headspace Analyses

Prior to evaluation in the environmental test chambers, materials are evaluated by headspace analysis. A sample of material is placed in a 1 liter Teflon-lined container that is purged with nitrogen at 50 ml/min for 30 min. The exit flow is collected on Tenax and analyzed after thermal desorption. Gas chromatography/mass spectroscopy (GC/MS) analysis identifies the compounds contained in the material's emissions. Approximately 10 of the compounds of highest concentration are selected for measurement in subsequent chamber tests.

Chamber Testing

Experimental designs are established for each material tested to evaluate the effect of various parameters: temperature, relative humidity, air exchange rate, and chamber loading. Prior to each test, the chambers are purged with clean air for several hours before placing samples in the chambers. Several types of materials have been evaluated, and the types of samples used in the chambers varied accordingly: silicone caulk, floor adhesive, and floor wax were spread on aluminum plates; wood stain was applied to a hardwood (poplar) board; and moth crystal cakes and particleboard were used "as is." The wood stain board and particleboard had their edges sealed with sodium silicate. The "wet" materials (caulk, adhesive, floor wax, and wood stain) were placed in the chamber shortly after being applied to the sample substrate. The test start (time = 0) was established when the door to the chamber was closed. The first sample was collected within 30 min. of the start. The samples were collected on Tenax/charcoal and analyzed by GC/FID. The organic species quantified depended on the results of the headspace analysis; total measured organics were also determined and recorded. The duration of each test depended on the type of material being tested; generally, tests were concluded when the same chamber concentration was observed for several measurements or when the analytical detection limits were reached.

EXPERIMENTAL RESULTS

Organic Compounds Identified

Table III shows representative organic compounds identified by headspace analysis for several materials.

Emission Rates

To determine the impact of indoor material/product sources on indoor concentrations of organic vapors, the emission rates for the various compound/source combinations are required. To date, such emission rate data have been developed only for formaldehyde from pressed wood products. The U.S. Department of Housing and Urban Development (HUD) has developed standards for formaldehyde emissions from pressed wood products used in mobile homes. These standards involve chamber testing of materials to determine compliance with emission restrictions. As part of the HUD regulation, the Berge equation is used to evaluate the chamber test results. The Berge equation relates formaldehyde concentration at standard conditions (i.e., 25°C, 50% relative humidity) to the test chamber concentration at different values of temperature and relative humidity.[11] The Berge equation predicts increasing emissions with increasing temperature and decreasing relative humidity. Matthews[12] and his co-workers at Oak Ridge National Laboratory have developed other models for determining formaldehyde emission rates that incorporate the following variables: temperature, relative humidity, air exchange rate, product loading, and formaldehyde concentration in the chamber. Matthews' models show that emission rates increase with increases in air exchange rate, decreases in product loading, and decreases in chamber concentration.

EPA's Air and Energy Engineering Research Laboratory conducted a cooperative project with Matthews to compare small chamber testing procedures for determining emissions from particleboard. Table IV provides emission rates for formaldehyde and other organics for various test conditions.[8] All tests were conducted at 23°C and 50% relative humidity on particleboard aged approximately 8 months. The emission rates in the bottom row of Table IV are representative of air exchange rates and loadings found in residential environments. Material newer than 8 months could be expected to have higher rates. The material tested was low density particleboard normally used in house construction (e.g., flooring material). Medium density particleboard, such as used in furniture, has formaldehyde emission rates two to four times higher.[12] Plywood products generally have lower emission rates than particleboard. Note that the formaldehyde emission rates are related to the air exchange and loading relationships discussed above. The emission rates for the other organic compounds do not vary substantially with these two parameters and appear to be limited by the rate of diffusion to the surface of the particleboard.

Limited research has been conducted on the emission rates of organics from materials other than pressed wood products. Molhave[4] conducted emission rate tests on 42 materials using a 1 m^3 test chamber with a ventilation rate of 1 air change per day. Girman et al.[13] evaluated emissions from 15 adhesives using 3.8 liter cans with an air exchange rate of 14 changes per hour. EPA has conducted emission tests on caulk, adhesive, floor wax, and wood stain using a 166 liter chamber at various air exchange rates. The Saskatchewan Research Council is testing emissions of caulking compounds. Georgia Tech Research Institute conducts chamber testing of building materials.

It is difficult to evaluate the limited data on emission rates of organic vapors from indoor materials/products because standard testing protocols have not been developed. A number of test conditions are critical to an effective determination of emission rates, including: temperature, relative humidity, air exchange rate, and product loading (area of sample/volume of test chamber). In addition, the effect of chamber concentration and chamber "wall effects" needs to be determined.[14] Finally, the age or condition of the sample affects emission rates. Any emission rate data must be coupled with a clear description of all of the variables and phenomena in order to evaluate and compare such data. To show the variability in reported emission rates, Table V compares emission rate data for two materials based on tests by three investigators.

For "wet" materials (such as floor adhesive and silicone caulk), time (or sample age) is a critical parameter. Figure 1 shows the emission factor of total measured organics from a silicone caulk over time for two air exchange rates. Note that the emission rate decreases rapidly with time as the volatile solvent materials are depleted from the caulk. Figure 1 also shows that emission rates are initially higher for the high air exchange rate (1.84/hr); after 2 hours, the rates are higher for the low air exchange rate (0.36/hr). Thus, the high air exchange rate caused the source to be depleted quicker.

Within the mixture of organic compounds emitted from a given source, the differences in emission factors for individual compounds can be quite large. Figure 2 shows emission factors over time for three of the compounds emitted from caulk. Note the differences in the emission rates between the compounds at any point in time; also, note that the ester and ketone emission rates decrease much faster than the rate of the alcohol. This time variation in emission factors for individual compounds will impact the indoor concentrations of these compounds over time.

MODELED CONCENTRATIONS

The emission rates shown in Figures 1 and 2 were calculated using source models developed to analyze data from small chamber tests. These models[14] provide rate constants for: source emissions, ventilation, chamber sink effects, and chamber concentration effects. The models can also be used to estimate the concentrations inside buildings due to the emissions from the materials or products tested. For example, Figure 3 shows the concentration vs. time for total organics that might be expected in a bathroom (14.5 m^3) after the application of 227 g (8 oz) of the silicone caulk discussed above. Figure 4 shows the estimated concentration vs. time history of three of the compounds emitted from the caulk. These figures illustrate the application of chamber test results to indoor environments. It is emphasized that these estimates assume building characteristics similar to the test chambers (i.e., complete mixing, equivalent sink effects, comparable air exchange). The models used to make these estimates have not yet been validated via test house or field study measurements.

CONCLUSIONS

Indoor organic vapors are emitted from a wide variety of materials and products. Small chamber testing can provide useful information on the emission rates. For "wet" materials, emission factors vary significantly with time. For a given material, emission factors for individual compounds can be quite different, and their variation over time may change. Source emission factors determined from chamber tests can be used in models to provide information on concentrations of organic vapors in indoor environments. Validation of this approach awaits experiments in test houses and the field.

REFERENCES

1. D. A. Sterling, "Volatile organic compounds in indoor air: an overview of sources, concentrations, and health effects," In: Gammage, R. B.; Kaye, S. B.; and Jacobs, V. A., eds. Indoor air and human health, Lewis Publishers, Inc., Chelsea, MI, 1985, pp. 387-402.

2. M. DeBortoli, H. Knoppel, E. Pecchio, A. Peil, L. Rogora, H. Schauenburg, H. Schlitt, and H. Vissers, "Concentrations of selected organic pollutants in indoor and outdoor air in northern Italy," Environ. Int. 12: 343-350 (1986).

3. E. Lebret, H. J. van de Wiel, H. P. Bos, D. Noij, and J. S. M. Boleij, "Volatile hydrocarbons in Dutch homes," Proceedings: 3rd International Conference on Indoor Air Quality and Climate, Swedish Council for Building Research, Stockholm, Sweden, 1984, pp. 169-174.

4. L. Molhave, "Indoor air pollution due to organic gases and vapours of solvents in building materials," Environ. Int., 8: 117-127 (1982).

5. V. B. Seifert, D. Ullrich, W. Mailahn, and R. Nagel, R., "Fluchtige organische verbindungen in der innenraunluft," Bundesgesundheitsblatt. 29: 417-424 (1986).

6. D. H. Steele, "Chlorocarbons - laboratory analysis of household products," Midwest Research Institute, Kansas City, MO, 1985.

7. L. A. Wallace, E. Pellizzari, T. Hartwell, M. Rosenzweig, M. Erickson, C. Sparacino, and H. Zelon, "Personal exposure to volatile organic compounds: I. Direct measurements in breathing-zone air, drinking water, food, and exhaled breath," Environ. Res. 8: 293-319 (1984).

8. L. H. Nelms, M. A. Mason, and B. A. Tichenor, "The effects of ventilation rates and product loading on organic emission rates from particleboard," In: Proceedings IAQ '86, American Society of Heating, Refrigerating, and Air-Conditioning Engineers, Inc., Atlanta, GA, 1986, pp. 469-485.

9. D. C. Sanchez, M. Mason, and C. Norris, "Methods and results of characterization of organic emissions from an indoor material", Atmos. Environ. 21: 337-345 (1987).

10. B. A. Tichenor and M. A. Mason, "Characterization of organic emissions from selected materials in indoor use," 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, Paper No. 86-16.5. 1986.

11. T. Godish and J. Rouch, "An assessment of the Berge equation applied to formaldehyde measurements under controlled conditions of temperature and humidity in a mobile home," J. Air Pollut. Control Assoc. 35: 1186-1187 (1985).

12. T. G. Matthews, "Modeling and testing of formaldehyde emission characteristics of pressed-wood products," Report XVIII to the U. S. Consumer Product Safety Commission, Oak Ridge National Laboratory Report No, ORNL/TM-9867, 1986.

13. J. R. Girman, A. T. Hodgson, A. S. Newton, and A. W. Winkes, "Emissions of volatile organic compounds from adhesives with indoor applications," Environ. Int. 12: 312-322 (1984).

14. J. E. Dunn and B. A. Tichenor, "Compensating for wall effects in IAQ chamber tests by mathematical modeling," 80th Annual Meeting of the Air Pollution Control Association, New York, Paper No. 87-83.4, 1987.

15. B. A. Tichenor, "Organic emission measurements via small chamber testing," Indoor Air '87, 4th International Conference on Indoor Air Quality and Climate, Berlin (West), Germany, 1987 (Paper accepted for presentation).

Table I. Typical solvent-based organic compounds found in indoor air.

Compound Class	Most Commonly Found Compounds
n-alkanes	nonane, decane, undecane
iso-alkanes	iso-octane, iso-nonane, iso-decane
cyclo-alkanes	cyclo-hexanes (various isomers, C-6 through C-9)
aromatics	benzene, toluene, xylene, trimethylbenzene
ketones	acetone, methyl ethyl ketone
alcohols esters	n-propanol, iso-propanol, n-butanol ethylacetate, butylacetate
aldehydes	pentanal, hexanal
terpenes	limonene
chlorinated compounds	carbon tetrachloride, dichloroethane, trichloroethane, dichloroethylene, trichloroethylene, tetrachloroethylene

Table II. Typical indoor sources of organic vapors.

Compound(s)	Material Source(s)
para-dichlorobenzene	moth crystals, room deodorants
methylene chloride	paint removers
chloroform	chlorinated water
formaldehyde	pressed wood products, foam insulation (UFFI), textiles, disinfectants
styrene	plastics, paints
toluene diisocyanate	polyurethane foam aerosols
phthalic acid anhydride, trimellitic acid, triethylene tetraamine	epoxy resins
sodium dodecyl sulfate	carpet shampoo
benzyl chloride, benzal chloride	vinyl tiles plasticized with butyl benzyl phthalate
ethylene oxide	sterilizers (hospitals)

Table III. Representative organic compounds identified via GC/MS.

Material/Product	Major Organic Compounds Identified
silicone caulk	methyl ethyl ketone, butyl propionate, 2-butoxyethanol, butanol, benzene, toluene
floor adhesive (water based)	nonane, decane, undecane, dimethyloctane, 2-methylnonane, dimethylbenzene
particleboard	formaldehyde, acetone, hexanal, propanol, butanone, benzaldehyde, benzene
moth crystals	p-dichlorobenzene
floor wax	nonane, decane, undecane, dimethyloctane, trimethylcyclohexane, ethylmethylbenzene
wood stain	nonane, decane, undecane, methyloctane, dimethylnonane, trimethylbenzene
latex paint	2-propanol, butanone, ethylbenzene, propylbenzene, 1,1'-oxybisbutane, butylpropionate, toluene
furniture polish	trimethylpentane, dimethylhexane, trimethylhexane, trimethylheptane, ethylbenzene, limonene
polyurethane floor finish	nonane, decane, undecane, butanone, ethylbenzene, dimethylbenzene
room freshener	nonane, decane, undecane, ethylheptane, limonene, substituted aromatics (fragrances)

Table IV. Emission Rates from Particleboard[a] (in ug/m^2 hr).

Air Exchange (hr^{-1})	Loading (m^2/m^3)	Formaldehyde	Acetone	Hexanal	Others[b]
2.71	1.96	154	37	15	27
0.54	1.17	95	41	26	26
3.61	0.78	230	38	20	31
0.54[c]	0.39[c]	140	37	24	27

[a] Particleboard was aged 8 months.
[b] The sum of emission rates for propanol, butanone, benzaldehyde, and benzene.
[c] Typical values for residences.

Table V. Organic emission rates for silicone caulk and floor adhesive.

Investigator	Chamber Volume (liter)	Air Exchange Rate (hr^{-1})	Time[a] (hr)	Material	Emission Factor (mg/m^2 hr)
Girman et al.[13]	3.8	14	-[b]	floor adhesive	140 - 180
Molhave [4]	1000	0.04	-[c]	floor adhesive	271
"	"	"	"	silicone caulk	26
Tichenor & Mason[10]	166	1.84	0.5	floor adhesive	1700
"	"	"	1	"	700
"	"	"	5	"	100
Tichenor[15]	"	"	0.5	silicone caulk	50
"	"	"	1	"	30
"	"	"	5	"	2

[a] The time elapsed since the sample was applied to the substrate.
[b] The sample was dried for 9 - 14 days prior to testing.
[c] The sample was brought to "equilibrium" prior to testing.

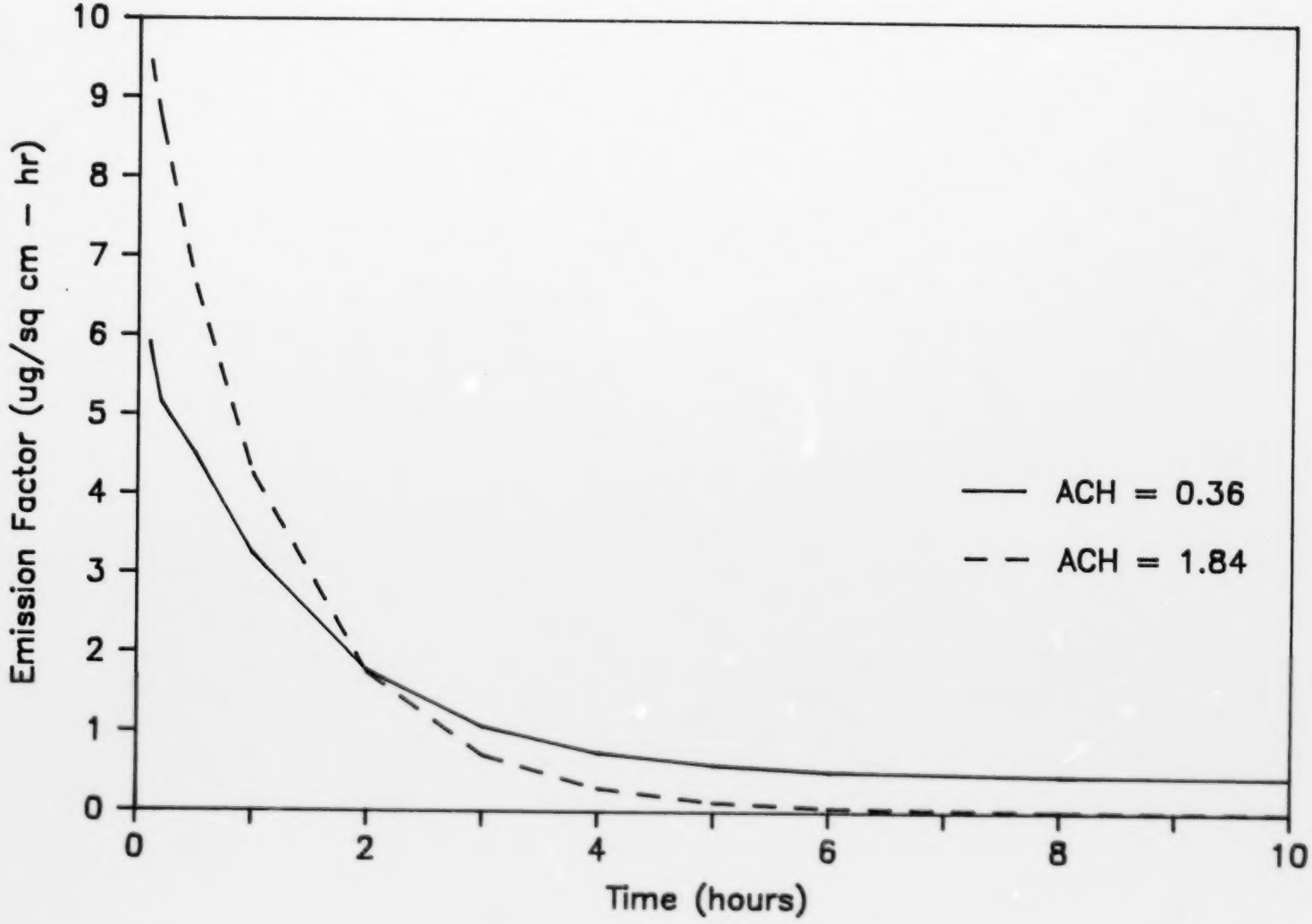

Figure 1. Emission Factor vs Time – Caulking Compound
Total Measured Organics

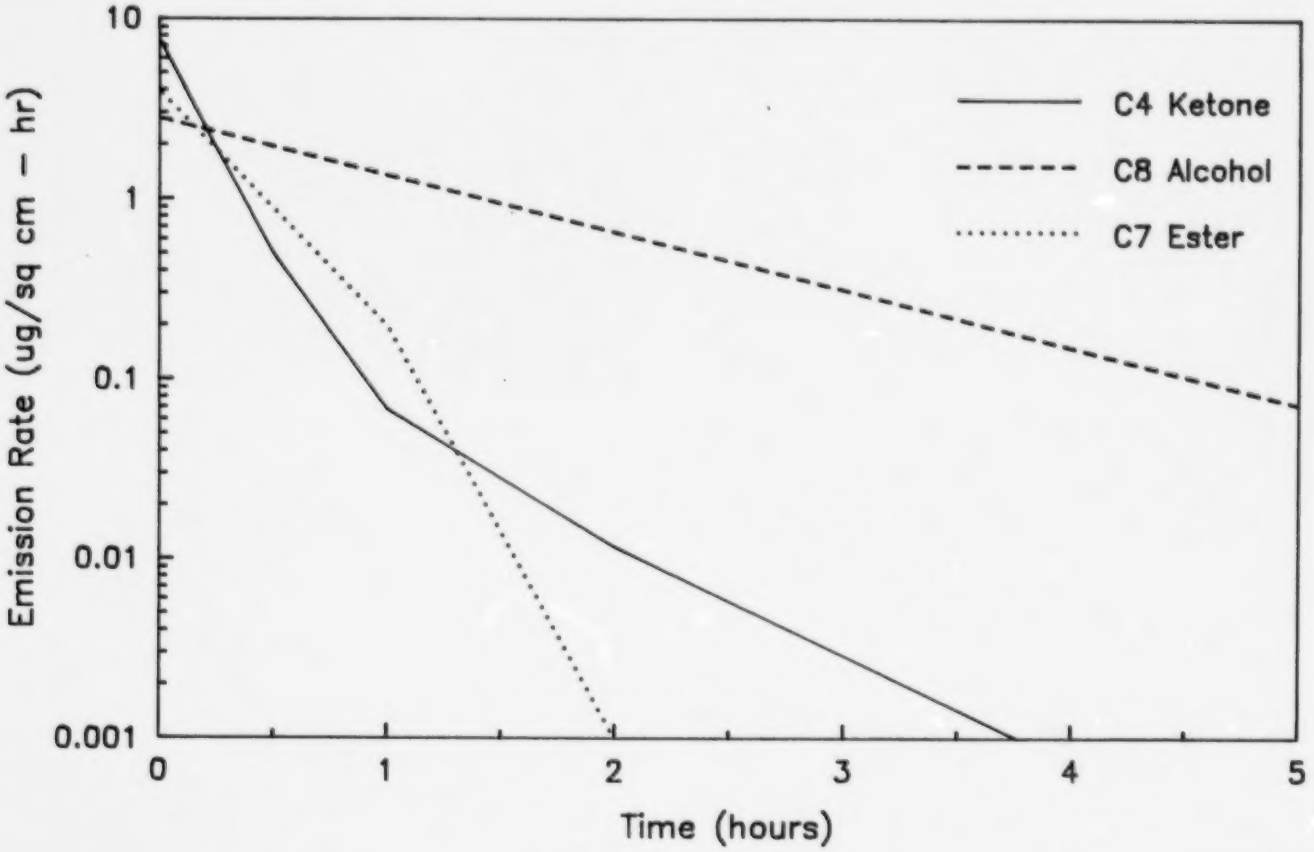

Figure 2. Caulk Emissions vs Time – Three Compounds

T = 23°C; RH = 50%; ACH = 1.84

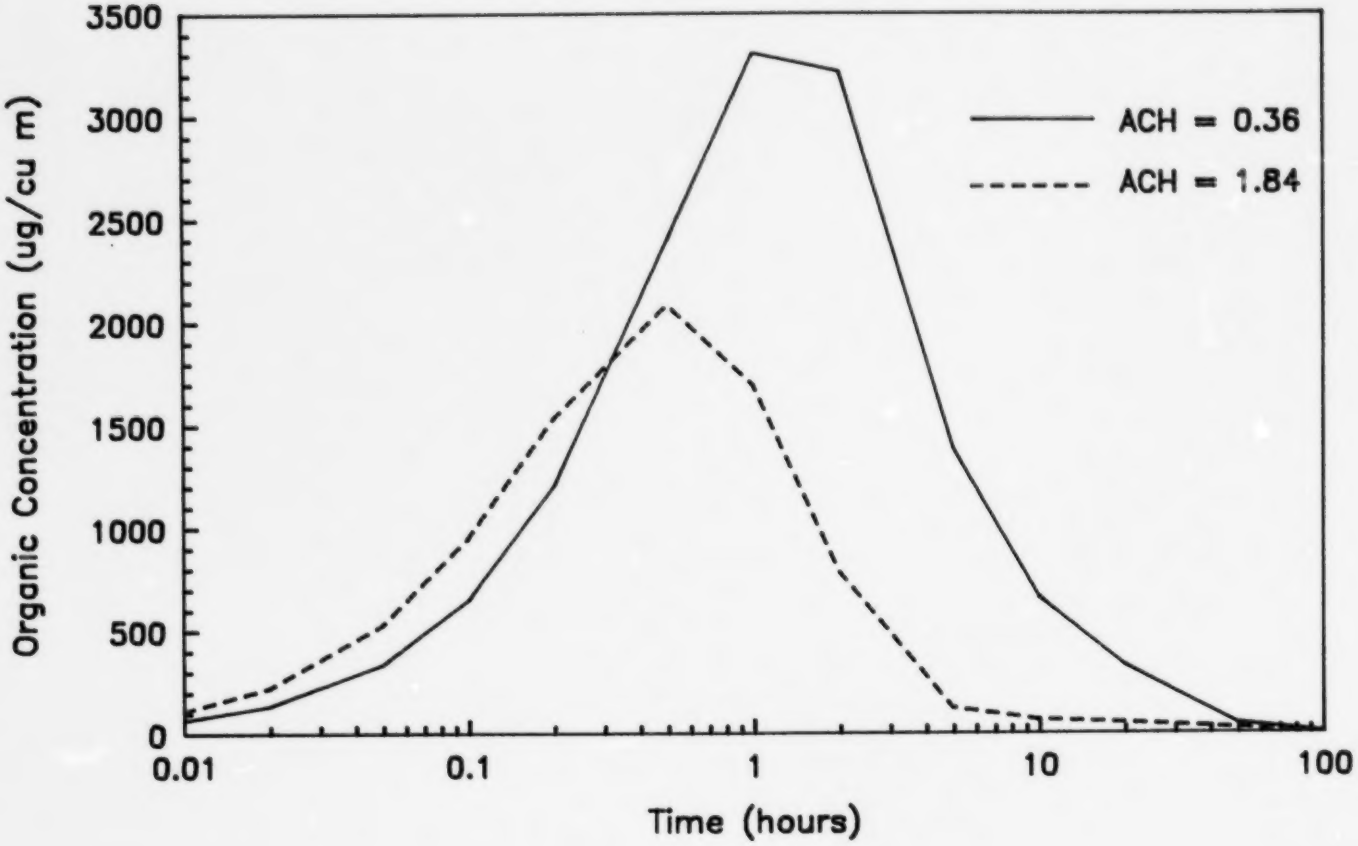

Figure 3. Total Organic Concentration vs Time
Silicone Caulk in Bathroom

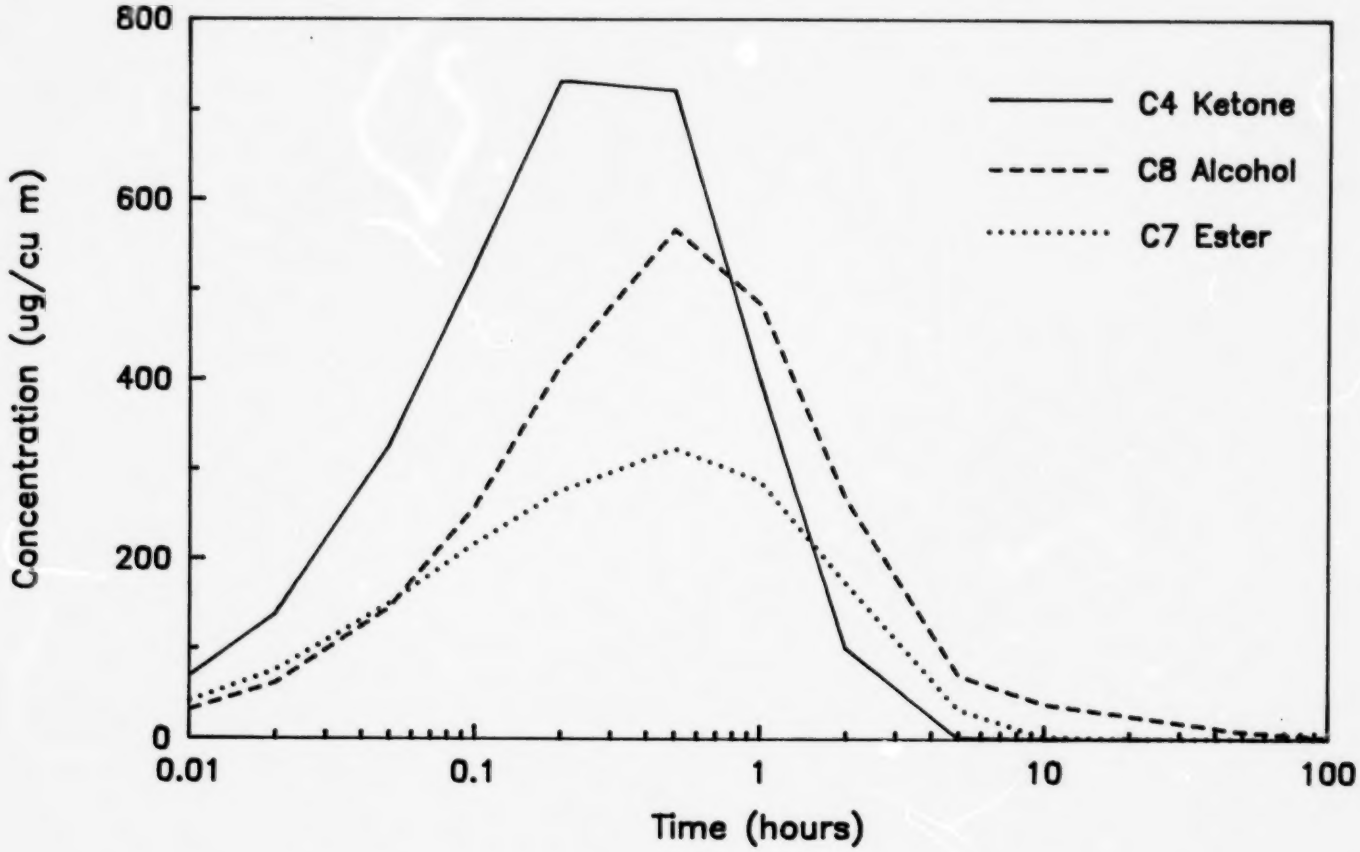

Figure 4. Concentration vs Time – Three Compounds
Silicone Caulk in Bathroom